

Alteration of GaInP₂ Energetics by Surface Modification to Achieve Photoelectrochemical Water
Splitting for Hydrogen Production

Todd Deutsch

DOE ERULF Program

Humboldt State University

National Renewable Energy Laboratory

Golden, Colorado 80401

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Participant: _____

Research Advisor: _____

Abstract

Photoelectrochemical splitting of water has been deemed the "holy grail" of electrochemistry. With that goal in mind, surface alteration of GaInP₂ semiconductors was undertaken to modify the energetics at the semiconductor/electrolyte interface. EDTA was used to modify the energetics to try to obtain favorable energetics and meet the criteria needed for photoelectrolysis. A positive shift of at least 300 mV is needed in order to achieve a working device. EDTA shifted the band edges negative by 50 mV and was therefore not an effective band shift reagent.

ERULF Chemistry

Humboldt State University

NREL

Ashish Bansal

303-275-3858

Ashish_Bansal@nrel.gov

Todd Deutsch

2467 Eye St. Apt. C

Arcata, CA 95521

707-826-0246

tgdl@axe.humboldt.edu

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Introduction

Increasing concern over global climate change due to greenhouse gas emissions has led us to examine the way energy is harnessed. There is expanding interest in using renewable sources to feed our energy demands. The intermittent nature of the most promising renewable technologies (solar and wind) requires an energy storage medium to provide power during times when the primary sources lie dormant. Some ways to store this captured energy are with batteries, pumped hydro, flywheels, or fuels. Batteries aren't practical for large scale use, pumped hydro is site dependent, flywheels lose energy with time, so fuels show the most promise for renewable energy storage. Hydrogen is a clean fuel which when used in a fuel cell produces only electricity, water, and a little heat. However, if hydrogen is obtained by the reformation or stripping of hydrogen from hydrocarbons, the term renewable does not apply. "Renewable" hydrogen can be produced by electrolyzing water with electricity produced from a renewable source. One renewable source that could provide the energy needed split water is photovoltaics. Hydrogen obtained this way and employed in a fuel cell represents a closed loop. This loop starts with sunlight and water and the final products are electricity and water (Figure 1). An energy economy based on this loop would not deplete our already plundered resources nor emit any pollutants into the environment. A hydrogen economy would also benefit national security because the energy would be produced from domestic sources. By eliminating our energy deficit we would no longer need to spend billions of dollars maintaining military control over politically unstable oil extracting regions.

Another advantage of hydrogen is that when "spilled", it will quickly diffuse into the atmosphere because it is the lightest element. This is in stark contrast to oil and gasoline. It is well known by the frequent crude oil spills the environmental havoc they can wreak. Hydrogen spilled from a personal vehicle would diffuse up and away from the accident site whereas gasoline puddles below creating a much more hazardous condition. Gasoline is also carcinogenic and poisonous, yet we bury thousands of gallons of it in tanks with our groundwater, keep at least 20 gallons in our garage, and make it available to any ten-year-old

with a dollar and a milk carton¹. Hydrogen is nontoxic and non-carcinogenic.

Calculations have been done by Turner to show that a hydrogen economy is feasible². We could provide energy for all our needs using just sunlight and water, two of the most abundant resources our earth has to offer. This system would have zero net emissions and last the lifetime of the sun. This is the technology that will power the future and it is in our hands today. There are still some technological hurdles in hydrogen production, storage, and utilization that need to be surmounted to make the hydrogen economy more practical and convenient. This clean and sustainable economy is clearly the impetus behind the research being conducted on hydrogen technologies.

It is the goal of this research to come up with a monolithic water splitting device that combines photovoltaics and electrolyzer into one unit. The objective is to split water directly on the surface of the semiconductor, thus eliminating the need for the most expensive part of the system, the electrolyzer (Figure 2). In addition, the elimination of interconnects and front contacts on the semiconductor can increase the overall efficiency of the conversion of sunlight to hydrogen.

It requires 1.23 eV to split water at room temperature. Once overpotentials at the anode and cathode are added to internal loss within the semiconductor, it requires a semiconductor with a bandgap of at least 1.7 eV in order to achieve water splitting. It is important that the bandgap not be much larger than that because of the inverse relationship between bandgap and range of solar spectrum absorbed by the semiconductor.

Not only is the magnitude of the bandgap essential for a working device, but so is the energetic position of the band edges. In order to produce oxygen and hydrogen, the band edges must encompass the hydrogen and oxygen redox potentials in water (Figure 3). In addition to these two criteria, the charge transfer at the semiconductor/electrolyte interface must be catalyzed in order to keep the band overlap criteria met under hydrogen and oxygen evolution conditions. Finally the semiconductor must be stable in an aqueous environment in order for the device to have a realistic lifetime.

GaInP₂ has a bandgap of 1.83 eV which makes it a good candidate for the water splitting reaction. Because a reducing environment is more favorable than an oxidizing one with respect to semiconductor surface stability, p-GaInP₂ is employed. Under light, this semiconductor injects photogenerated electrons into the solution producing hydrogen. Previous studies have shown, however, that the flatband potential of this system is 0.10 to 0.40 eV too negative for the water splitting reaction to occur³. These flatband potentials are capable of being changed though.

The Helmholtz layer is the layer of molecules adjacent to the semiconductor/electrolyte interface. The energetic position of the flatband is dependent on the charge within this Helmholtz inner layer. This correlation is what causes the flatband potential at the interface to be dependent on pH. Previous studies have reported a 55 meV/pH correlation which is a result of varying the net charge within the Helmholtz layer³. Adding positive charges such as H⁺ has the effect of shifting the bands more positive. Adding negative charges such as OH⁻ has the opposite effect. To this end, the buildup of uncatalyzed electrons adds negative charges to the semiconductor/electrolyte interface and shifts the bands in the negative, or undesired direction. This presents the problem that even if optimal band edge position is achieved in the dark, charge transfer at the semiconductor/electrolyte interface must be catalyzed in order to keep the band edges in the same energetic position under light. There are various techniques which can modify the energetics and kinetics of the reaction of interest.

One way to move the band positions is by using a multijunction solid state device. These tandem cells provide a potential boost by incorporating two different photovoltaic semiconductors into one device. This heterogeneous semiconductor relies on a GaAs solar cell to provide the voltage boost needed to bring the flatbands of the p-GaInP₂ top layer into the overlap condition. Previous studies at NREL on monolithic tandem p-nGaAs/TJ/p-GaInP₂ structure showed it capable of splitting water but it was unstable in an aqueous medium⁴. Kocha and Turner revealed another way that the band edge position can be displaced, through semiconductor surface modification. They found GaInP₂ band edges could be shifted 0.30 eV positive by adsorbing 8-quinolinol onto the surface⁵. This study showed that surface

modification of the semiconductor could adjust the energetics of the bands to the desired positions.

The goal of this research is to shift the bands sufficiently positive by surface adsorption of dipoles. By adsorbing the positive end of polar molecules on the surface, the net charge in the Helmholtz layer should be more positive and therefore shift the bands positively. Impedance spectroscopy performed on electrodes immersed in dilute solutions of organic molecules revealed positions of the band edges. From evaluation of these positions, correlation between surface treatment and energetics of the GaInP₂/electrolyte interface was drawn.

Experimental

The p-GaInP₂ epilayers were grown here at NREL by atmospheric pressure organometallic vapor-phase epitaxy on GaAs substrates with zinc as the dopant. The 2.5 μm GaInP₂ layers were grown on Zn doped 2□(110) GaAs substrates. The carrier concentration in the GaInP₂ was about $5 \times 10^{17} \text{ cm}^{-3}$. Ohmic contacts were made by the electrodeposition of gold onto the unpolished back side of the substrates. The wafers were then cut into pieces about .25 mm² and connected to copper wire via conducting silver paint(Colloidal Silver Liquid, Ted Pella Inc). After the silver paint had dried in the oven at 80□C for an hour, the sides and back of the electrode were coated with a non-conducting epoxy (Hysol 9462, Dexter Corp). This resulted in an electrode with only the front surface of the semiconductor exposed that was typically 0.1-0.2 cm².

The surface treatment of the electrodes consisted of simply immersing the electrode in diluted (0.01M) solutions of the molecule to be tested and performing cyclic voltammetry. All solutions were made containing 0.2 M K₂SO₄ as the supporting electrolyte. The electrode was etched in concentrated H₂SO₄ for 20 seconds, rinsed, and dried under a stream of nitrogen immediately preceding immersion into a new solution. The pH of each solution was determined using a Cole-Parmer pH/mV/□C meter in addition to pH strips. All chemicals used were reagent grade and made with in-house deionized water.

The electrochemical measurements were made using a three electrode cell with platinum gauze as the counter electrode and a saturated calomel electrode (SCE) as the reference. A 150 W tungsten-halogen fiber optic illuminator was used to illuminate the samples for light readings. Current-voltage (I-V) and Capacitance-voltage (C-V) data was collected using a Solartron SI 1287 Electrochemical Interface connected to a Solartron SI 1260 Impedance/Gain-Phase Analyzer. The C-V and I-V measurements were made at a frequency of 10 KHz with a 20 mV AC amplitude and a scan rate of 20 mV/s. The potential ranged typically from -1.0 to +0.3 V vs. SCE for the dark measurements and was extended up to -2.0 V for some light measurements. The slope and x-intercept of the Mott-Schottky ($1/C^2$ Vs V) plots was used to determine dopant density and flatband potentials.

[1]Turner, John A. A Practical Route to Our Renewable Energy Future. *Environmental Review*. 7(5): 1-8; 2000.

[2]Turner, John A. A Realizable Renewable Energy Future. *Science*. 285(5427): 687-689; 1999.

[3]Kocha, S. S., Turner, J. A., Nozik, A. J. *Electroanal. Chem.*, 367, 27 (1994).

[4]Kocha, S. S., Montgomery, D., Peterson, M., Turner, J. A. 1998. Photoelectrochemical decomposition of water utilizing monolithic tandem cells. *Solar Energy Materials and Solar Cells* 52: 389-397.

[5]Kocha, S. S., Turner, J. A. 1995. Displacement of the Bandedges of GaInP₂ in Aqueous Electrolytes Induced by Surface Modification. *J. Electrochem. Soc.* 142(8): 2625.

| | | | | | avg | pH |
|-----------------------------------|-----------|-----------|--------|--------|------------|----|
| TD071900GIP115EDTApH1DA RK | -4.99E+15 | -4.94E+15 | 0.611 | 0.609 | 0.6101785 | 1 |
| TD072400GIP116pH1EDTADA RK | -7.52E+15 | -7.32E+15 | 0.609 | 0.617 | 0.613321 | 1 |
| TD072400MB284pH1EDTADAR K | -1.79E+16 | -1.72E+16 | 0.616 | 0.630 | 0.623239 | 1 |
| TD071800GIP115pH4buffdark | -5.51E+15 | -5.43E+15 | 0.463 | 0.492 | 0.47753 | 4 |
| TD071900GIP115pH4BUFFDAR K | -5.13E+15 | -5.08E+15 | 0.444 | 0.475 | 0.45939 | 4 |
| TD072400GIP116pH4BUFFDAR K | -7.42E+15 | -7.34E+15 | 0.422 | 0.478 | 0.4498265 | 4 |
| TD071800GIP115EDTApH5DA RK | -5.14E+15 | -4.93E+15 | 0.379 | 0.448 | 0.4136045 | 5 |
| TD072000GIP115EDTApH5DA RK | -5.26E+15 | -5.05E+15 | 0.387 | 0.445 | 0.4159765 | 5 |
| TD072100-EDTApH5-DARK | -4.88E+15 | -4.67E+15 | 0.384 | 0.443 | 0.413648 | 5 |
| TD072400GIP116pH5EDTADA RK | -7.28E+15 | -7.06E+15 | 0.350 | 0.450 | 0.3998535 | 5 |
| td071800gip115pH7buffdark | -5.40E+15 | -5.04E+15 | 0.370 | 0.479 | 0.424282 | 7 |
| TD072400MB284pH7BUFFDAR K | -1.83E+16 | -1.75E+16 | 0.374 | 0.449 | 0.4113365 | 7 |
| TD071800GIP115pH11BUFFDA RK | -5.34E+15 | -4.82E+15 | 0.194 | 0.349 | 0.271929 | 10 |
| TD072400GIP116pH10BUFFDA RK | -7.87E+15 | -7.13E+15 | 0.248 | 0.409 | 0.328489 | 10 |
| TD072400MB284pH10BUFFDA RK | -1.83E+16 | -1.64E+16 | 0.234 | 0.429 | 0.331839 | 10 |
| TD071900GIP115EDTApH11DA RK | -4.98E+15 | -4.65E+15 | 0.109 | 0.202 | 0.155183 | 11 |
| TD072400GIP116pH11EDTADA RK | -7.78E+15 | -6.89E+15 | 0.125 | 0.353 | 0.239139 | 11 |
| TD072400MB284pH10EDTADA RK | -1.84E+16 | -1.61E+16 | 0.165 | 0.358 | 0.261594 | 11 |
| TD072400GIP116pH14BUFFDA RK | -5.01E+15 | -4.81E+15 | -0.180 | -0.121 | -0.150227 | 14 |
| TD072400GIP116pH14EDTADA RK | -4.88E+15 | -4.69E+15 | -0.204 | -0.143 | -0.1735755 | 14 |
| TD072000GIP115EDTApH5LT0. 01mA | -5.11E+15 | -4.87E+15 | 0.176 | 0.228 | 0.2019475 | 5 |
| TD072000GIP115EDTApH5LT0. 02mA | -5.19E+15 | -4.65E+15 | 0.160 | 0.234 | 0.196669 | 5 |
| TD072000GIP115EDTApH5LT0. 05mA | -5.26E+15 | -4.57E+15 | 0.133 | 0.229 | 0.181151 | 5 |
| TD072000GIP115EDTApH5LT0. | -5.53E+15 | -4.36E+15 | 0.011 | 0.193 | 0.10171225 | 5 |

10mA

| | | | | | avg | pH |
|---------------------------|-----------|-----------|--------|--------|------------|----|
| TD071800GIP115pH4buffdark | -5.51E+15 | -5.43E+15 | 0.463 | 0.492 | 0.47753 | 4 |
| td071800gip115pH7buffdark | -5.40E+15 | -5.04E+15 | 0.370 | 0.479 | 0.424282 | 7 |
| TD071800GIP115pH11BUFF | -5.34E+15 | -4.82E+15 | 0.194 | 0.349 | 0.271929 | 10 |
| DARK | | | | | | |
| TD072400GIP116pH14BUFF | -5.01E+15 | -4.81E+15 | -0.180 | -0.121 | -0.150227 | 14 |
| DARK | | | | | | |
| TD071800GIP115EDTApH5D | -5.14E+15 | -4.93E+15 | 0.379 | 0.448 | 0.4136045 | 5 |
| ARK | | | | | | |
| TD071900GIP115EDTApH11 | -4.98E+15 | -4.65E+15 | 0.109 | 0.202 | 0.155183 | 11 |
| DARK | | | | | | |
| TD071900GIP115EDTApH1D | -4.99E+15 | -4.94E+15 | 0.611 | 0.609 | 0.6101785 | 1 |
| ARK | | | | | | |
| TD072400GIP116pH14EDTA | -4.88E+15 | -4.69E+15 | -0.204 | -0.143 | -0.1735755 | 14 |
| DARK | | | | | | |
| TD071900GIP115EDTApH1D | -4.99E+15 | -4.94E+15 | 0.611 | 0.609 | 0.6101785 | 1 |
| ARK | | | | | | |
| TD072400GIP116pH1EDTAD | -7.52E+15 | -7.32E+15 | 0.609 | 0.617 | 0.613321 | 1 |
| ARK | | | | | | |
| TD072400MB284pH1EDTAD | -1.79E+16 | -1.72E+16 | 0.616 | 0.630 | 0.623239 | 1 |
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| TD071800GIP115EDTApH5D | -5.14E+15 | -4.93E+15 | 0.379 | 0.448 | 0.4136045 | 5 |
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| TD072000GIP115EDTApH5D | -5.26E+15 | -5.05E+15 | 0.387 | 0.445 | 0.4159765 | 5 |
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| TD072100-EDTApH5-DARK | -4.88E+15 | -4.67E+15 | 0.384 | 0.443 | 0.413648 | 5 |
| TD072400GIP116pH5EDTAD | -7.28E+15 | -7.06E+15 | 0.350 | 0.450 | 0.3998535 | 5 |
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| DARK | | | | | | |
| TD072400GIP116pH11EDTA | -7.78E+15 | -6.89E+15 | 0.125 | 0.353 | 0.239139 | 11 |
| DARK | | | | | | |
| TD072400MB284pH10EDTAD | -1.84E+16 | -1.61E+16 | 0.165 | 0.358 | 0.261594 | 11 |
| ARK | | | | | | |
| TD072400GIP116pH14EDTA | -4.88E+15 | -4.69E+15 | -0.204 | -0.143 | -0.1735755 | 14 |
| DARK | | | | | | |
| TD071800GIP115pH4buffdark | -5.51E+15 | -5.43E+15 | 0.463 | 0.492 | 0.47753 | 4 |
| TD071900GIP115pH4BUFFD | -5.13E+15 | -5.08E+15 | 0.444 | 0.475 | 0.45939 | 4 |
| ARK | | | | | | |
| TD072400GIP116pH4BUFFD | -7.42E+15 | -7.34E+15 | 0.422 | 0.478 | 0.4498265 | 4 |
| ARK | | | | | | |
| td071800gip115pH7buffdark | -5.40E+15 | -5.04E+15 | 0.370 | 0.479 | 0.424282 | 7 |
| TD072400MB284pH7BUFFD | -1.83E+16 | -1.75E+16 | 0.374 | 0.449 | 0.4113365 | 7 |
| ARK | | | | | | |
| TD071800GIP115pH11BUFF | -5.34E+15 | -4.82E+15 | 0.194 | 0.349 | 0.271929 | 10 |
| DARK | | | | | | |
| TD072400GIP116pH10BUFF | -7.87E+15 | -7.13E+15 | 0.248 | 0.409 | 0.328489 | 10 |

| | | | | | | | |
|------------------------|------|-----------|-----------|--------|--------|------------|----|
| | DARK | | | | | | |
| TD072400MB284pH10BUFFD | | -1.83E+16 | -1.64E+16 | 0.234 | 0.429 | 0.331839 | 10 |
| | ARK | | | | | | |
| TD072400GIP116pH14EDTA | | -4.88E+15 | -4.69E+15 | -0.204 | -0.143 | -0.1735755 | 14 |
| | DARK | | | | | | |